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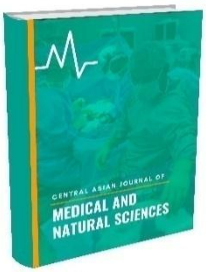

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Immobilized Organic Luminescent Reagents for the Determination of Certain Heavy Metals

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Annotation: Luminescent reagents for the determination of aluminum, beryllium, zinc, tungsten, thorium, and lead are proposed. Completed immobilization investigated organic compounds and a positive effect is shown on their chemical and analytical properties. New organic reagent-carrier systems for solid-phase luminescent determination of aluminum, beryllium, zinc, tungsten, thorium, and lead are proposed. Highly sensitive and selective methods of sorption-luminescent determination of the studied metals in environmental objects have been developed.

Keywords: immobilization, toxic metals, organic compounds, sorption-luminescent determination.

One of the global environmental problems today is the pollution of environmental objects. High industrial growth rates and large production volumes have led to increased human impact on the environment. With the intensification of production methods, the involvement of toxic elements in the biogeochemical cycle has increased. Among the many consequences of human society, the process of progressive accumulation of metals in the environment is of particular importance. The most dangerous pollutants include heavy and toxic metals [1]. In this regard, the importance of rapid reliable analytical monitoring of the state of environmental objects becomes obvious. In this aspect, the development of rapid and sensitive methods for the determination of toxic metals is promising.

Recent studies have shown the potential of using optical chemical sensor devices for rapid determination of metals in environmental objects [2-4]. Their action is based on performing reactions of detectable substances with chromophore reagents in conditions and forms that allow obtaining a visually observable and easily measurable effect using optical detection methods [1-10].

Detection is usually performed by solid-phase spectroscopy [3] or by the luminescent method [4]. The luminescence intensity or diffuse reflection coefficient is measured directly from the solid surface of the immobilized reagent or its complex compound with metal ions [5]. The luminescent method is promising in this respect due to its high sensitivity and relatively inexpensive hardware design [2].

The sensitive layers of optical sensor devices are organic reagents immobilized on solid matrices. The role of organic reagents is reduced to the concentration and determination of inorganic and organic molecules. Sorption concentration followed by detection from a solid matrix reduces the detection limit by several orders of magnitude [7-9], and the use of sorbents modified with organic reagents makes it possible to increase the selectivity of the analysis [10]. The principles of immobilization have already been formulated and the development trends in this area are clearly presented. Theoretical [11] and methodological [12] aspects of immobilization are considered in the literature.

A number of methods for the determination of elements by immobilized organic reagents are proposed, both in the photometric [13-15] and luminescent versions [16-18].

For the determination of low metal contents, luminescent reagents belonging to various classes of organic compounds are known: polyoxyflavones [19], hydroxyanthroquinones [20], oxyazo compounds [21], etc.

Based on the available data on the use of organic reagents in the analysis of a number of metals [22-23], as well as from the results of studying the structures and preliminary studies of a number of organic reagents [24], the following oxiazo compounds were selected as objects of research: calcocarboxylic acid, eriochrome red B, eriochrome gray SQL, eriochrome blue SE, eriochrome blue-black R polyoxyflavone-morin; hydroxyanthroquinone – carminic acid.

The aim of this work is to establish the effect of immobilization on the chemical and analytical properties of luminescent organic reagents and to develop based on them sorption-luminescent methods for the determination of aluminum, beryllium, zinc, lead, thorium and tungsten in environmental objects and food products.

Methods and materials:

Standard solutions of beryllium and aluminum, of zinc with a concentration of 1 mg / ml was prepared by dissolving the corresponding metal sample (qualification "h. h." in dilute (1:1) hydrochloric acid "oc. h." according to [25]. A standard lead solution with a concentration of 1 mg / ml was prepared by dissolving a high-purity metal in HCl and HNO_3 "osch" [25]. A tungsten solution with an approximate concentration of 1 mg / ml was prepared by dissolving the sample $Na_2WO_3*H_2O$ marks "H. H." in 0.5 n. NaOH. The titer of the solution was determined gravimetrically by precipitation WO_3^- [25]. The titer of the resulting solution is 0.8659 mg / ml. A thorium solution with an approximate concentration of 1 mg / ml was prepared by dissolving thorium nitrate. The titer of the solution was determined by complexometry EDTA with alizarin red C. The titer of the solution was 0.9166 mg / ml. Working solutions were prepared by appropriate dilution with bidistillate of the initial standard solution.

Working solutions of organic reagents were prepared by appropriately diluting the initial standard metal solutions with bidistillate. $1x10^{-3}$ molar solutions of calcocarboxylic acid, red B eriochrome, blue-black eriochrome R, blue-black B eriochrome, grey's eriochrome SGL(R_3), blue eriochrome SE, kapminic acid was prepared by dissolving exact samples of preparations in water. $1x10^{-3}$ a molar solution of morin was prepared by dissolving a sample of the drug in ethanol.

We used freshly harvested and peeled po [26] solvents and bidistillate, deionized water, previously checked for the absence of luminescence.

Equipment. The electronic absorption spectra of the reagent solutions under study and their complex compounds with beryllium and aluminum ions were recorded on a SF-46 spectrometer in cuvettes with l=1 cm with a deuterium lamp and an incandescent lamp.

The excitation and luminescence spectra were recorded at UV spectrofluorimeter Agilent Cary Eclipce and an SDL-2 spectrometer with a MS 0507 computer, as well as an installation consisting of an ISP-51 spectrograph with glass optics, a FEP-1 photoelectric set-up with a FEU-19 photomultiplier and a KSP-4 self-recording potentiometer and. Filtered DKSH-150 radiation was used as the excitation source. To obtain a curve for the distribution of radiation energies, depending on the wavelength, the installation was graded using a reference incandescent lamp with a known color temperature of 2850 K and correction coefficients were found for each wavelength. All intensity values for fluorescence were obtained taking into account the spectral sensitivity of the device to PMT. IR spectra were recorded on a spectrophotometer UR-10 (Karl Zeiss, Jena) spectrometer "Analitrsystem 360 FT-IR"firms "Nikolet Justrument Corporation"(US) in tablets KBr, LiF, in the solution $CHCl_3$ and others in the range of 500-4000 cm^{-1}.

A pH meter was used to measure pH. «METTLER TOLEDO», calibrated according to standard buffer solutions in the medium of the solvent in which the determination was performed (DMF, DMSO, IPS, ethanol). The pH values for buffer mixtures in the H medium were used$_2$0-DMFA, N$_2$0-ethanol listed in the paper [27]. The solutions were pumped using a PP-2-15 peristaltic pump.

Results and discussion

The complexation of aluminum with calcocarboxylic and carminic acids and eriochrome gray was studied SQL, eriochrome blue SE; beryllium with calconcarboxylic acid, eriochrome red B, carminic acid; lead with eriochrome red B and eriochrome blue-black R; zinc with eriochrome red in and eriochrome blue-black In. Complexation in each metal-reagent system was studied by plotting curves: luminescence intensity – pH, buffer mixture composition, organic solvent content, organic reagent concentration, discharge order, and time. The research results are shown in Table 1 and Figure 1.

Table 1. Optimal conditions for complexation of organic reagents with the studied metals

System	Metal	λfl., nm	pH range	vol. % org. of solvent	Time of fluorescence development, min
Calcone-Carboxylic acid	Ve	453	9.0-11.0	40 (DMFA)	10
	Al	553	4.0-4.6	50 (DMFA)	15
Eriochorom red In	Ve	530	5.5-7.5	60 (DMFA+ ethanol)	10
	Pb	520	5.5-6.5	28.5 (DMFA)	10
	Zn	530	5.5-7.5	20 (DMFA)	20
Eriochrome blue-black R	Pb	540	4.0-4.5	57.1 (DMFA)	20
Eriochrome Grey SGL	Al	545	5.0-7.5	30 (DMFA)	8
Eriochrome blue-black In	Zn	530	4.5-8.0	40 (DMFA+ ethanol)	15
Carminic Acid	Al	530	4.5-5.5	57 (DMSO)	20
	Ve	582	4.0 – 4.5	33 IPS	20

To determine the mechanism of complexation of organic reagents with metal ions under study, the ratios of the incoming components were determined by the methods of isomolar series and saturation, the number of displaced protons, the charge of the complex, and the particles forming the complexes.

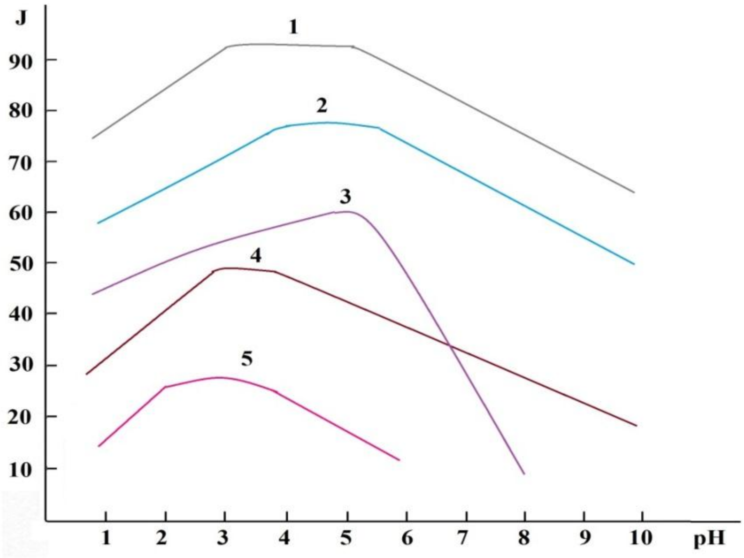

Figure 1. *The dependence of the fluorescence intensity of the complex from the acidity of the medium by immobilization: 1 - eriochrome blue SE on Molselect 72 G-10; 2 – eriochrome red on Sephadex G-10; 3 - eriochrome blue-black on Molselect 72 G-50; 4 - eriochrome blue-black R on Sephadex G-25; 5 - eriochrome grey SGL on Molselect 72 G-25.*

The main chelating groups involved in the formation of the quasi-aromatic metal-chelate cycle are determined based on the obtained results, IR spectra, and comparison of literature data.

To improve the chemical and analytical properties using pre-sorption concentration, the possibility of immobilization of calcocarboxylic acid, red B eriochrome, and gray eriochrome was studied SGL, blue eriochrome SE, blue-black eriochrome R, blue-black B eriochrome, carminic acid, and morin on various types of sorbents [28-29].

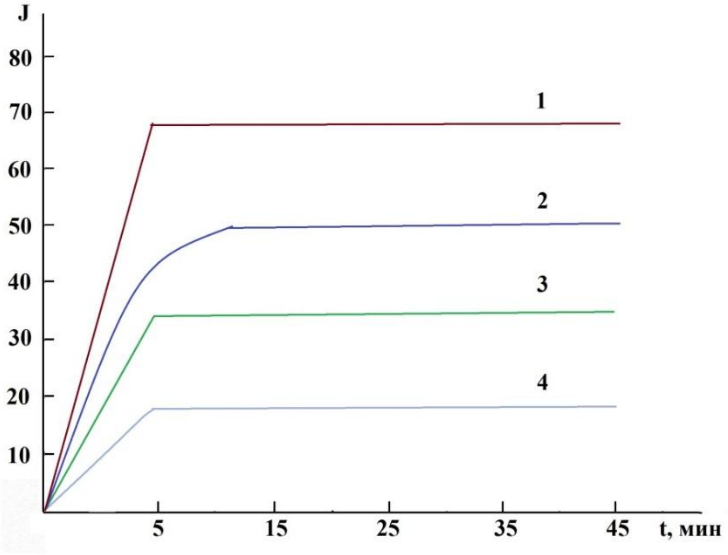

Figure 2. *Dependence of the fluorescence intensity on the contact time of the reagent-carrier: 1- eriochrome red B-Molselect 72 G-15; calcocarboxylic acid on Amberlit XAD-2; 3 – carminic acid-Silasorb-600; 4 - carminic acid - Flor e sil*

Studies have shown the suitability for immobilization of calcocarboxylic acid-AmberlitXAD-2; for eriochrome red B – MolselectG-15; for eriochrome gray SGL-Molselect 72 G-25; for eriochrome blue SE-Molselect 72 G-10; for eriochrome blue-black R-SephadexG-25; for eriochrome blue-black B – Molselect 72 G-50; for immobilization of carminic acid - magnesium silicate Floresil, as well as modified silica Silasorb-600; for immobilization of morin – Sephadex G 15-120 (Fig. 2).

Optimization of the immobilization conditions was performed by determining the maximum analytical signal with varying acidity, reagent concentration in solution, and reagent-carrier contact time. To select the optimal concentration of reagents during immobilization, the "load" of the carrier was determined [30]. The" load " of the carrier was determined by the residual concentration of reagents above the precipitate using the spectrophotometric method. The results of the studies are shown in table 2.

Table 2. Optimal conditions for immobilization of the studied reagents

m_H=0.4 g

Reagent	Media source	pH of the medium	Buffer mixture volume , ml	Carrier "load", mcg/g	Contact time , min.
Calconcarbonic acid	AmberlitXAD-2	1.0-3.0	3.0	19.72	10
Eriohoromkrasny In	Molselect 72 G-15	3.5-5.0	4.00	636.00	5
Eriochrome blue-black R	SephadexG-25	3.0-4.0	3.00	226.38	5
Eriochrome grey SGL	Molselect 72 G-25	2.5-3.5	3.00	116.0	5
Eriochrome blue-black In	Molselect 72 G-50	3.5-5.5	3.00	589.5	5
Eriochrome blue SE	Molselect 72 G-10	3.0-5.0	3.00	158.7	5
Carminic Acid	Silasorb-600	8.0-14.0	1.00	30.64	5
	Floresil	6.5-7.5	2.00	295.71	5
Maureen	Sephadex G 15-120	1 n HCl	2.0	873.72	5

Determination of the protolytic properties of organic reagents in solution and in the immobilized state and comparison of data allowed us to show the advantages of immobilization. To assess changes in the donor-protolytic characteristics of reagents in the immobilized state, the absorption and luminescence spectra were studied at various pH values. It is shown that the protolytic properties of organic reagent molecules significantly change due to photoexcitation and the process of immobilization, which leads to a redistribution of electron density. The pH limits in which the ionic forms of reagents are in equilibrium are determined.

The results showed that the electron-donating properties of oxyazo compounds increase by 2-3 orders of magnitude compared to the ground state, and in the excited state by 0.81-0.83 orders of magnitude compared to the immobilized excited state. The electron-donating properties of polyoxyflavones increase by 1.32 orders of magnitude compared to the ground state, and in the excited state by 1.5 orders of magnitude compared to the immobilized excited state. Thus, the immobilization process makes a significant contribution to the change in protolytic properties, which significantly determines the acidity of the formation of luminescent complexes of the studied metals with immobilized reagents.

The conditions of complexation of immobilized reagents with the studied ions are studied. The results are shown in Table 3. The analytical parameters of complexation of the studied ions with immobilized reagents and with reagents in solution are compared.

Table 3. Optimal conditions for complexation of immobilized cells reagents with the studied metals

System	Metal	λfl., nm	HRN interval	vol. % org. solvent content	Fluorescence development time, min
Calcone-carboxylic acid-AmberlitXAD-2	Ve	490	7.5-10.0	15	20
	Al	555	3.0-4.0	50 (DMFA)	10
Eriochorom red In-Molselect 72 G-15	Ve	530	3.5-7.0	–	Immediately after merges
	Pb	520	3.5-5.0	14.2	5
	Zn	525	3.0-5.5	15 (DMFA)	5
Eriochrome blue-black R-SephadexG-25	Pb	520	3.0-4.0	28.5	10
Eriochrome grey SGL-Molselect 72 G-25	Al	525	2.0-4.0	15 (DMFA)	5
Eriochrome blue-black In-Molselect 72 G-15	Zn	515	3.5-6.5	10 (DMFA)	10
Eriochrome Blue SE-Molselect 72 G-10	Al	515	3.0-5.0	15 (ethanol)	15
Carminic Acid - Silasorb-600	Al	525	2,0-4,0	28.6 (ethanol)	10
Carminic Acid-Floresil	Ve	620	5,0-8,0	32 (DMFA	5
Maureen- Sephadex G 15-120	W	535	1M NSl	-	Immediately after merges
	Th	540	0.1 M NSl	-	5

Comparison of the spectral and fluorescent characteristics of metal complexation with the studied reagents in solution and in the immobilized state showed that for complex compounds of immobilized reagents, the Stokes shift decreases in comparison with complexes in solution. This indicates that the value of the quantum of absorbed energy and the quantum of energy converted to luminescent energy began to differ less. Consequently, the structures of metal complexes with the studied reagents became more rigid, which is confirmed by an increase in the quantum number of yield of complex compounds with an immobilized reagent compared to complexes in solution. This is associated with a reduction in the detection limit of beryllium and aluminum using the proposed new analytical systems.

Comparison of the optimal values of the acidity of complexation of aluminum, beryllium, lead, and zinc with the studied reagents in solution and with the immobilized reagents shows that the optimal pH value shifts by 2 units to the acidic region for beryllium complexes with immobilized calcocarboxylic acid and eriochrome red B compared to complexation in solution. There is a shift of the optimal pH value by 1-3 units to the acidic region for aluminum complexes with immobilized calc carboxylic acid, eriochrome gray SGL and eriochrome blue SE compared to complexation in solution. Optimal value of the acidity of complexation of immobilized red B eriochrome with lead and zinc, as well as lead with immobilized blue-black eriochrome R and zinc with immobilized blue-black eriochrome B is shifted by 1-2 units. to the acidic area compared to complexation in solution. This explains a significant improvement in the selectivity of metal determination by immobilized reagents compared to reagents in solution. It is important to note that the proportion of the organic phase as a result of immobilization of reagents decreased by 60 times for the beryllium complex with red eriochrome B; by 2-3 times for beryllium complexes with calcocarboxylic acid, lead with red eriochrome B and eriochrome blue-black R; for the zinc complex with eriochrome red B, the proportion of the organic phase decreased by 1.5 times and for the zinc complex with eriochrome blue-black by 4 times. The time of development of fluorescence was reduced by 2-10 times, i.e. the expressiveness of the developed methods increased [31].

Considering the above data, we can conclude that the immobilization of calcocarboxylic acid, red B eriochrome, blue-black eriochrome R, blue-black B eriochrome, gray eriochrome SGL, blue eriochrome SE carminic acid and morin led to an improvement in the metrological characteristics of complex compounds of reagents with aluminum, beryllium, lead, and zinc ions in comparison with complexes in solution.

To characterize the selectivity of reactions, numerous experiments were carried out to elucidate and eliminate the interfering effect of a number of elements on the correct determination of aluminum, beryllium, lead, zinc, tungsten, and thorium. Summing up the results obtained on the effect of various amounts of metal ions on the accuracy of determination of the studied metals and the possibility of masking, the maximum permissible amounts of extraneous ions (selectivity factor) are found. The results showed that when using immobilization and masking mixtures, the selectivity of the complexation reaction is significantly improved compared to the reactions in solution.

Based on the studied complexation reactions, methods for the quantitative determination of aluminum, beryllium, zinc and lead, tungsten and thorium by immobilized calcocarboxylic acid, red B eriochrome, and blue-black eriochrome have been developed R, eriochrome blue-black B, eriochrome gray SGL, eriochrome blue SE, carminic acid and morin. Intervals of proportional dependence between the fluorescence intensity and the concentration of metal ions are found. The method of mathematical statistics is used to evaluate the correctness of the performed definitions. The limit of detection of metals by immobilized reagents is reduced in comparison with detection in solution (Table 4).

Table 4. Comparison of sensitivity of determination of the studied metals by oxy-azo compounds in solution and in the immobilized state.

Metal	Reagent	Detection limit, mcg / ml	
		in solution	in the immobilized state
Aluminum	calcocarboxylic acid acid	0.400	0.040
	carminic acid	0.140	0.014
	eriochrome blue SE	0.004	0.0001
	eriochromic gray SGL	0.01	0.0002
Beryllium	calcocarboxylic acid acid	0.007	0.0007
	eriochrome red B	0.008	0.0006
	carminic acid	0.100	0.020

Lead	eriochrome red B	0.005	0.0006
	eriochrome blue-black R	0.028	0.0028
Zinc	eriochrome red B	0.026	0.0016
	eriochrome blue-black In	0.487	0.012
Tungsten	Maureen	0.003	0.0001
Thorium	Maureen	0.02	0.001

Based on the studied complexation reactions, methods for quantitative sorption-fluorimetric determination of metals in natural and waste waters, as well as in food products, are proposed.

Conclusion

The positive effect of immobilization on the chemical and analytical properties of oxyazo compounds is shown.

Based on the studied complexation reactions, rapid, sensitive, and selective methods for the quantitative sorption-luminescent determination of aluminum, beryllium, zinc, and lead by immobilized reagents in environmental objects and food products are proposed.

The advantage of the proposed sorption-luminescent methods for the determination of metals is the ability to determine them directly from the surface of immobilized reagents after sorption concentration.

The proposed reagent-carrier systems can be proposed as sensitive layers of optical sensor devices for the determination of aluminum, beryllium, zinc and lead.

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